Adiabatic Connection in the Low-Density Limit

Zhenfei Liu and Kieron Burke
Department of Chemistry, University of California, Irvine, California, 92697-2025
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In density functional theory (DFT), the exchange-correlation functional can be exactly expressed by the adiabatic connection integral. It has been noticed that as $\lambda \to \infty$, the λ^{-1} term in the expansion of $W(\lambda)$ vanishes. We provide a simple but rigorous derivation to this exact condition in this work. We propose a simple parametric form for the integrand, satisfying this condition, and show that it is highly accurate for weakly-correlated two-electron systems.

In density functional theory (DFT) [1], the exchange-correlation functional $E_{\rm XC}[n]$ is exactly expressed by the adiabatic connection [2, 3] formula:

$$E_{\rm XC}[n] = \int_0^1 d\lambda\, W[n](\lambda), \tag{1}$$

where λ is a coupling constant that connects the Kohn-Sham system ($\lambda = 0$) to the true system ($\lambda = 1$), while keeping the density $n(\mathbf{r})$ fixed. The integrand, $W(\lambda)$, contains only potential contributions to $E_{\rm XC}$. The shape of $W(\lambda)$ has been much studied in DFT [4]. For example, the success of hybrid functionals that mix some fraction of exact exchange with a generalized gradient approximation (GGA) can be understood this way [5]. There is ongoing research to use the low density ($\lambda \to \infty$) limit as information in construction of accurate models of $W(\lambda)$ [6, 7, 8]. Recently, the adiabatic connection formula has been used directly in functional construction [9].

The expansion of $W(\lambda)$ in the high-density (weak coupling) limit for finite systems is known to be [7]:

$$W(\lambda) = W_0 + W_0'\lambda + \cdots \text{as } \lambda \to 0, \tag{2}$$

where $W_0' = 2E_{\rm C}^{\rm GL2}$, with $E_{\rm C}^{\rm GL2}$ the second-order coefficient in Görling-Levy perturbation theory [6, 10, 11]. The expansion in the low-density (strongly correlated) limit is believed to be [7, 12]:

$$W(\lambda) = W_\infty + W_\infty'\lambda^{-1/2} + \cdots \text{as } \lambda \to \infty, \tag{3}$$

where W_∞' is defined as the coefficient of $\lambda^{-1/2}$ in the expansion above, and W_∞ can be calculated from the strictly correlated electron (SCE) limit [13]. In addition to these expansions, by definition the exact $W[n](\lambda)$ is known to satisfy the following scaling property [7]:

$$W[n](\lambda) = \lambda W_1[n_{1/\lambda}], \tag{4}$$

where $n_{1/\lambda}(\mathbf{r})$ is the scaled density, defined by $n_\gamma(\mathbf{r}) = \gamma^3 n(\gamma\mathbf{r})$, $0 < \gamma < \infty$. In the equations above, one can show that $W_0 = E_{\rm x}$, the exchange energy, and that W_∞ is finite [6]. The dependence on $\lambda^{-1/2}$ in the low-density limit is because correlation dominates here, and the Thomas-Fermi screening length is proportional to $\lambda_F^{-1/2}$.

In practical DFT calculations, $W(\lambda)$ must be approximated. However, any approximate $W(\lambda)$ should satisfy several exact conditions, such as Eqs. (2), (3) and (4). In the erratum to Ref. [7], Seidl et al. concluded that for the ISI model (see below), the spurious $\lambda^2 \ln\lambda$ term in $E_{\rm C}[n_\lambda]$ is due to the λ^{-1} term in the expansion of $W(\lambda)$ as $\lambda \to \infty$ [Eq. (3)]. In a recent work [12], this was proved rigorously, but only by calculating zero-point oscillations about the strictly-correlated limit. In this paper, we provide a simple derivation and how this exact constraint affects approximate functionals. Throughout this paper, we use atomic units ($e^2 = \hbar = \mu = 1$) everywhere, i.e. all energies are in Hartrees and all distances in Bohr radii.

Any λ-dependence can always be expressed in terms of density scaling. Using the fundamental relation of Levy-Perdew equation [14], one finds:

$$W[n](\lambda) = E_{\rm x}[n] - \gamma^2 \frac{d}{d\gamma}\left(\frac{E_{\rm C}[n_\gamma]}{\gamma^2}\right), \tag{5}$$

and it is generally believed for nondegenerate Kohn-Sham systems [15] that $E_{\rm C}[n_\gamma]$ has the following expansion in the low density limit ($\gamma \to 0$):

$$E_{\rm C}[n_\gamma] = \gamma\left(B_0[n] + \gamma^{1/2}B_1[n] + \gamma B_2[n] + \cdots\right), \tag{6}$$

where the $B_k[n]$'s ($k = 0, 1, 2\cdots$) are scale-invariant functionals. Substituting into Eq. (5), we find the expansion of $W(\lambda)$ for large λ:

$$W(\lambda) = E_{\rm x}[n] + B_0[n] + \frac{1}{2}\lambda^{-1/2}B_1[n] - \frac{1}{2}\lambda^{-3/2}B_3[n] + \cdots \tag{7}$$

i.e. the λ^{-1} term is missing, and $W(\lambda)$ is independent of $B_2[n]$.

Now we survey approximations to $W(\lambda)$ and see whether they have the correct low-density expansion [Eq. (7)]. There are several kinds of approximations, the most famous being the ISI (interaction-strength interpolation) model by Seidl et al [6, 7, 8]:

$$W^{\rm ISI}[n](\lambda) = W_\infty[n] + \frac{X[n]}{\sqrt{1 + Y[n]\lambda} + Z[n]}, \tag{8}$$

where $X = xy^2/z^2$, $Y = xX/z^2$, $Z = X/z - 1$, with $x = -2W_0'[n], y = W_\infty'[n]$, and $z = E_{\rm x}[n] - W_\infty[n]$.

The ISI model uses the values of $W[n]$ and its derivatives at both the high-density ($\lambda \to 0$) and the low-density ($\lambda \to \infty$) limits, to produce an accurate curve

for $W(\lambda)$, $0 \le \lambda \le 1$, to insert in Eq. (1) to get an approximation to $E_{\rm XC}$. It gives very accurate results for the correlation energy [7] and meets several conditions. But if we expand $W^{\rm ISI}$ in the low density limit:

$$W^{\rm ISI}(\lambda) = W_\infty + \frac{X}{\sqrt{Y}}\lambda^{-1/2} + \frac{XZ}{Y}\lambda^{-1} + \cdots , \qquad (9)$$

we can see that its λ^{-1} term does not generally vanish, although it works very well numerically for $E_{\rm C}$ [16]. This wrong coefficient was already shown to produce a spurious term ($\lambda^2 \ln \lambda$) in the expansion of $E_{\rm C}[n_\lambda]$ as $\lambda \to \infty$ [7].

There were several attempts to overcome this problem [correctly omitting the λ^{-1} term but including all the other (integer and half-integer powers) terms] in the literature [12, 17] by modifying the ISI model, but they are less simple: one requires W_0'' [the next order in Eq. (2)] [17] and the other is not a direct model to W_λ [12]. Consider instead the following 4-parameter interpolation model:

$$W^{\rm acc}(\lambda) = a + by + dy^4, \qquad y = \frac{1}{\sqrt{1+c\lambda}}, \qquad (10)$$

where a, b, c, and d are scale-invariant functionals. We use the same inputs as those for the ISI model, i.e. W_0, W_0', W_∞, and W_∞', to fit the parameters. Generally there are no analytical expressions in compact form for the parameters, and one has to solve for them numerically. The 4th power in y is the lowest that can be added while satisfying the exact conditions, but producing an expansion with non-zero λ^{-n} terms ($n \in \mathbb{Z}, n > 1$). We recommend use of this $W^{\rm acc}$ to replace the ISI model because it is numerically accurate and avoids the λ^{-1} term in the low-density limit. One can show that $W^{\rm acc}$ obeys the scaling property [Eq. (4)], provided that $W_0[n_\gamma] = \gamma W_0[n]$, $W_0'[n_\gamma] = W_0'[n]$, $W_\infty[n_\gamma] = \gamma W_\infty[n]$, and $W_\infty'[n_\gamma] = \gamma^{3/2} W_\infty'[n]$, as they should. If we integrate $W^{\rm acc}(\lambda)$ over λ from 0 to 1, we find a simple expression for the exchange-correlation energy:

$$E_{\rm XC}^{\rm acc} = a + \frac{d}{1+c} + 2b(-1+\sqrt{1+c})/c. \qquad (11)$$

We compare the performance of the new model and ISI on Hooke's atom, two electrons in a spherical harmonic well, with force constant $k = 1/4$. We show below that for this system, our $W^{\rm acc}$ works as a highly-accurate interpolation, even more accurate than the ISI model.

Magyar et al. [18] calculated the $W(\lambda)$ curve for $0 \le \lambda \le 4$ for Hooke's atom ($k = 1/4$) using $W_0 = E_{\rm X} = -0.515$ and $W_0' = -0.101$ as inputs. They confirmed that $W_\infty = -0.743$, consistent with the SCE ansatz [6]. They also found $W_\infty' = 0.235$, but this was based on a fit that violated our condition, so we discount this result. Gori-Giorgi [19] calculated $W_\infty' = 0.208$ based on the SCE model [6, 12], which we consider exact. We apply these inputs (W_0, W_0', W_∞, and W_∞') to our $W^{\rm acc}$ and the ISI model ($W^{\rm acc}$ generates two sets of solutions for a, b, c, and d, but we select the one with d closest to b, for it can be reduced to $W^{\rm simp}$ as below). We plot the differences between these models and the exact curve (taken from Ref. [18]) in Fig. 1. One can see that our $W^{\rm acc}$ works very well between $\lambda = 0$ and 1, which is the range of interest. Its predictions for W_1', $E_{\rm C}$, and $E_{\rm C} + T_{\rm C}$ are excellent, with $T_{\rm C}$ being the correlation energy from the kinetic part, as listed in Table I. With these exact inputs, we found that, as $\lambda \to \infty$, $W^{\rm ISI} \to -0.743 + 0.208\lambda^{-1/2} + 0.068\lambda^{-1} + \cdots$, which shows that although the coefficient of λ^{-1} is small, it does not vanish.

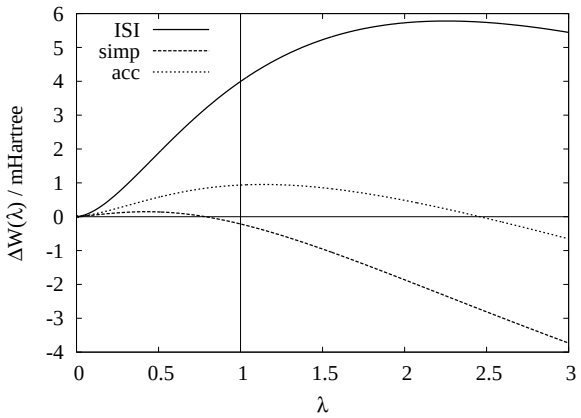

FIG. 1: Comparison of three different approximations to $W(\lambda)$ for Hooke's atom ($k = 1/4$), plotted as $\Delta W = W^{\rm model} - W^{\rm exact}$. The exact curve (up to $\lambda = 3$) is taken from Ref. [18].

TABLE I: Comparison of several quantities for three different approximations to $W(\lambda)$ for Hooke's atom ($k = 1/4$). The exact values are taken from Ref. [18] except for W_∞' [19]. All energies are in mHartrees.

	exact	ISI	simp	acc
W_1	-583	-579	-583	-582
W_1'	-44	-41	-45	-44
$E_{\rm C}$	-39	-37	-38	-38
$E_{\rm C} + T_{\rm C}$	-10	-10	-9	-9

We can also apply our $W^{\rm acc}$ to the helium atom. Here $W_0 = E_{\rm X} = -1.025$, $W_0' = -0.095$ [20], and $W_\infty = -1.500$ [6], $W_\infty' = 0.621$ [12] from the SCE model [6, 12]. We plot the differences between these models and the exact curve (taken from Ref. [21]) in Fig. 2 and compare several key quantities in Table II.

One can see that our model here works fairly well, and $W^{\rm simp}$ (see below) is even a little better than $W^{\rm acc}$. ISI does not satisfy the exact condition we derived in this

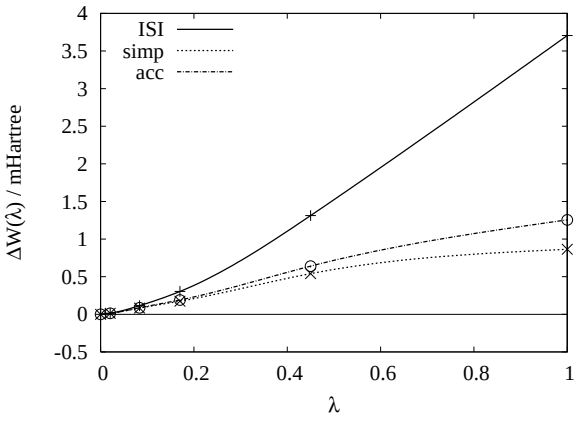

FIG. 2: Comparison of three different approximations to $W(\lambda)$ for helium atom, plotted as $\Delta W = W^{\rm model} - W^{\rm exact}$. The discrete values are shown, as well as fitting curves to aid the eyes. $W^{\rm exact}$ values (up to $\lambda = 1$) are taken from Ref. [21].

TABLE II: Comparison of several quantities for three different approximations to $W(\lambda)$ for helium atom. The exact values are taken from Ref. [21]. All energies are in mHartrees.

	exact	ISI	simp	acc
W_1	-1104	-1100	-1103	-1103
W_1'	-64	-60	-64	-63
$E_{\rm C}$	-42	-40	-42	-41
$E_{\rm C}+T_{\rm C}$	-6	-6	-5	-5

work [Eq. (7)]: as $\lambda \to \infty$, $W^{\rm ISI} \to -1.500 + 0.621\lambda^{-1/2} + 0.376\lambda^{-1} + \cdots$, so the λ^{-1} coefficient is not even small.

Now, we propose a simpler version of $W^{\rm acc}$, which cannot be used in typical cases, as the exact value of W_∞' is not known in general. A simpler model is constructed by setting $d = b$, to yield:

$$W^{\rm simp}(\lambda) = a + b(y + y^4), \qquad y = \frac{1}{\sqrt{1+c\lambda}}, \qquad (12)$$

with a, b and c being scale-invariant functionals. We have found (see results for Hooke's atom and helium atom) that although there is one parameter less, the above form produces usefully accurate results, especially between $\lambda = 0$ and 1. In a word, $W^{\rm acc}$ acts as an accurate interpolation to the whole adiabatic connection curve, while $W^{\rm simp}$ is more convenient and practical to use, without losing accuracy. It yields $W_\infty' = 0.191$ for Hooke's atom and 0.594 for helium.

We use W_0, W_∞ and W_0' to construct the explicit form of $W^{\rm simp}(\lambda)$, and find:

$$a = W_\infty, \quad b = \frac{W_0 - W_\infty}{2}, \quad c = \frac{4W_0'}{5(W_\infty - W_0)}. \qquad (13)$$

Thus a and b set the endpoints, while c is a measure of the curvature. Substituting Eq. (13) into Eq. (12), we get the explicit form of $W(\lambda)$ in terms of W_0, W_∞ and W_0'. One can show that it has the correct expansion in both limits, and it obeys the scaling property [Eq. (4)]. Setting $d = b$ in Eq. (11) and subtracting exchange, it yields:

$$E_{\rm C}^{\rm simp} = 2b[f(c) - 1], \quad f(c) = [\sqrt{1+c} - \frac{1+c/2}{1+c}]/c, \qquad (14)$$

with b and c defined in Eq. (13). $E_{\rm C}^{\rm simp}$ correctly recovers GL2 in the weakly-correlated limit ($W_\infty \to -\infty$, keeping W_0 and W_0' fixed, such as in the $Z \to \infty$ limit of two-elecron ions) and $E_{\rm XC}^{\rm simp}$ correctly reduces to W_∞ for strong static correlation ($W_0' \to -\infty$, keeping W_0 and W_∞ fixed, such as for stretched H_2). We can calculate the kinetic correlation energy $T_{\rm C}$:

$$T_{\rm C} = b[2f(c) - z - z^4], \qquad (15)$$

with $f(c)$ defined in Eq. (14) and $z = 1/\sqrt{1+c}$, showing that the curvature $\beta = T_{\rm C}/|E_{\rm C} - T_{\rm C}|$ [22] is a function of c alone. We strongly urge $E_{\rm XC}^{\rm simp}$ be applied whenever its inputs are accurately known.

We can further test our $W^{\rm simp}$ in systems with more than two electrons, but only those for which all inputs are known, with results listed in Table III. One can see that $W^{\rm simp}$ predicts $E_{\rm C}$ fairly accurately, but is less accurate than $W^{\rm ISI}$. This is perhaps due to lack of W_∞' in $W^{\rm simp}$.

TABLE III: Comparison of $W^{\rm simp}$ and $W^{\rm ISI}$ on systems with more than two electrons. $E_{\rm X}$, W_0' and W_∞ are taken from Ref. [13], and W_∞' is taken from Ref. [12]. All energies are in Hartrees.

	$E_{\rm X}$	W_0'	$W_\infty^{\rm SCE}$	$W_\infty'^{\rm SCE}$	$E_{\rm C}^{\rm ISI}$	$E_{\rm C}^{\rm simp}$	$E_{\rm C}^{\rm exact}$
Be	-2.67	-0.250	-4.02	2.59	-0.104	-0.110	-0.096
Ne	-12.1	-0.938	-20.0	22.0	-0.410	-0.432	-0.394

In fact, in their first paper on the ISI model, Seidl et al. proposed a similar model [6], which yields results numerically very close to those of ISI, but without the y^4 term. But their model contains no $\lambda^{-n} (n > 1)$ contributions. Note that none of these models work for the uniform electron gas, because $W_0' = -\infty$ [16], so both the model developed by Seidl et al. [6] and $W^{\rm simp}$ reduce to $W(\lambda) = W_\infty$.

After the bulk of this work was completed, we received a preprint of Ref. [12], containing a detailed theory of the leading corrections to $W(\lambda)$ as $\lambda \to \infty$, consistent with the much simpler arguments given here. Also, we

use their W'_∞ value for helium (see text) to replace the old one predicted by point-charge-plus-continuum (PC) model [7].

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